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Chlorine Distribution in the Idaho Batholith

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Chlorine is thought to play a major role in the mobilization and concentration of base metals in the formation of ore deposits. The regional distribution of chlorine in the Idaho Batholith was studied to see if this could be related to mineralization or metallic provinces. One hundred forty-eight whole-rock samples, mineral separates, and standards were analyzed for chlorine by x-ray fluorescence. The mean value for whole rock samples was 380 ppm. Counting error for one standard deviation averaged 8%. The standard deviation, including sampling error, was under 16%. Only three whole rock samples had chlorine significantly above the mean.

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CHLORINE DISTRIBUTION IN THE IDAHO BATHOLITH

by

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The expected concentration of chlorine in the biotite fraction was not found. The chlorine was not significantly water leachable from the whole rock samples following normal grinding. The Idaho Batholith as a source for mineralizing chlorine was not established.

The chlorine distribution supports, but does not prove, a metamorphic origin for the Idaho Batholith. Cretaceous and possibly tertiary thermal events may have homogenized the chlorine in the batholith. Since chlorine seems to be so widely available in source rocks, a better way to correlate its presence to mineralization would be to study the residual chlorine from the ore deposition process.

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INTRODUCTION

The purpose of this thesis is to investigate the possible relationship between epigenetic silver-gold-copper-lead-zinc deposits and the regional chlorine content of associated country rock. The central hypothesis is that high chlorine availability in the country rock facilitates the mobilization and concentration of base metals in solutions which may often form base metal mineral deposits, and conversely, that inadequate chlorine availability will reduce the amount of ore produced in an area or region. Another basic assumption is that the availability of chlorine depends on the amount and type of bonding of the chlorine in the country rock or intrusives in the area or region of the ore deposits. This thesis attempts to determine whether chlorine concentration in country rock is a limiting factor of ore formation in portions of the Idaho Batholith. Areas with insufficient available chlorine in the country rock and intrusives should be barren of base metal ore, but lack of available chlorine is far from the only reason for lack of ore.

Jerome (1967) and Noble (1970) have studied the distribution of metal deposits in the western United States. Noble defines a metal ore deposit province which in part cuts across the Idaho Batholith. An important part of this thesis is to see if this metal province correlates with a high chlorine content. An alternative hypothesis, that metal provinces represent areas with metal-rich country rock or intrusives, has failed a number of tests (Flinter, 1972; Tilling, 1973).

To avoid making this introduction prohibitively long, several topics with which economic geologists are probably already familiar are included in Appendix A. The material included in this appendix is the result of considerable library research by the writer and may well be helpful in providing background for those less familiar with the field of economic geology. This appendix includes a discussion of the following topics:

1. Some prevalent theories of hydrothermal ore genesis.
2. Distribution of base metals in country rock.
3. Distribution of chlorine in country rock.
4. Data from fluid inclusions.
5. Laboratory experiments.
6. Field evidence.

PREVIOUS WORK

I. GENERAL

Apart from some early Russian references (Sokolov, 1964; Komarov, 1965; Sokolov, 1966), the first important article on the possible role of chlorine in prospecting for base metal deposits was by Stollery (1971). He measured chlorine in biotite along a two kilometer section of the lead-zinc mineralized Providencia Stock, Zacatecas, Mexico. The biotites averaged 2,500 to 5,000 ppm chlorine, about two to three times the mean of granitic rock biotites. The bulk rock analyses averaged 700 ppm chlorine which is high by a similar factor. The biotites were analyzed by electron microprobe and the whole rock by atomic absorption following dissolution. Mention is made of other granites with equally high chlorine which are not mineralized, however. The evidence suggests that chlorine is nearly uniform across small intrusives, and that high chlorine may encourage ore formation but does not guarantee it.

Parry (1972) used electron microprobe analyses to compare the chlorine in biotites from mineralized and unmineralized stocks in Nevada and Utah. A correlation of mineralization with copper in the biotite but not lead or zinc was found. Biotites from mineralized plutons had 1,000 to 4,000 ppm chlorine. Biotites from unmineralized plutons had, with one exception, 0 to 2,000 ppm chlorine. There were not enough samples to determine the statistical significance of these findings.

Kesler (1973) tried to correlate mineralization with the water soluble chloride in granodioritic rocks from the Caribbean and Central America. Ion-selective electrodes were used for the analysis. The mean values for stocks ranged from 14 to 217 ppm with large standard deviations. It was not possible to distinguish the mineralized stocks from the unmineralized ones.

Studies of the salinity of fluid inclusions by Nash (1973) showed that chloride correlates well with copper, gold and bismuth anomalies near the Copper Canyon, Utah deposits. The chloride is more localized than the pyritized zone and is therefore a more specific exploration guide in this case.

Jacobs (1973) studied several porphyry copper deposits with regard to chlorine as well as fluorine, magnesium, and titanium. He found 100 to 4,500 ppm chlorine (usually under 2,000 ppm) in primary, altered, and hydrothermal biotites. Chlorine is lost through chloritization or hydrothermal alteration of primary minerals. He found that chlorine content did not differentiate mineralized from non-mineralized plutons.

Most recently, Kesler (1973) analyzed 100 biotites from Central and North America for chlorine, fluorine, and water. Chlorine was analyzed by ion-selective electrodes following fusion and dissolution. Biotites from barren plutons had 0-1600 ppm chlorine while those from mineralized plutons had 0-2600 ppm chlorine. The conclusion was that 45% of barren plutons had biotites with under 200 ppm chlorine. Individual intrusive systems were found to have a characteristic chlorine content. Kesler

concluded chlorine content could only be used as an adjunct to other geochemical methods as an exploration tool.

As indicated in the discussion of lateral secretion in Appendix A, intrusives are not necessarily the source of chloride for ore deposits associated with the intrusives. The chloride could be brought in by circulating ground water. This may be one reason why the correlation of ore deposits with the chlorine content of associated intrusives is low.

II. IDAHO BATHOLITH

There are a number of theories for the origin of the Idaho Batholith (Schmidt, 1957). Discussions in this thesis assume that the Idaho Batholith is composite igneous-metamorphic but predominately metamorphic, derived mostly from sedimentary rocks and intruded by usually small igneous stocks (Schmidt, 1957; Swanberg, 1973). The primary evidence is the striking linearity of many major rock units in the batholith. Some geologists believe the batholith is predominately of igneous origin. The term batholith will be used in a local traditional sense, not a genetic one. The late Tertiary stocks and plutons within the Idaho Batholith share several chemical (Swanberg, 1973), spatial, and temporal (Anderson, 1951) characteristics. The contribution of chlorine to their ore potential is thus less masked by other factors than the essentially unrelated plutons studied by Parry (1972).

Trapped saline solutions in the pre-metamorphic rocks and solutions generated by metamorphism probably moved predominantly upward and outward during metamorphism. Wasserstein (1947) found that marginal

granites of a batholith had higher values (0.1-0.3%) of fluorine than the more deeply eroded center (0.05% and less). Fluorine and chlorine are chemically similar enough that chlorine might be expected to show a similar pattern in this environment. In some cases, such as the Salton Sea brines, semi-permeable rocks such as shales may have acted to produce brines by hyperfiltration of dilute pore waters (Helgeson, 1968).

This thesis proposes to examine variations in chlorine content on a regional scale within a unit of mostly common genesis. Since Stollery (1971) found little variation in chlorine across the two mile wide Providencia stock, Zacatecas, Mexico, five miles was chosen as a sampling interval for the Idaho Batholith. The results may provide a useful background trend for any studies of more localized areas in the region.

The Idaho Batholith extends about 240 miles north to south and 85 miles east to west in west-central Idaho and a small part of western Montana. Predominant rock types are granodiorite to quartz monzonite. Although the Idaho Batholith is poorly mapped due to the rugged topography, it is known to be composed of five major rock types which comprise about 95% of its exposed surface. These are: coarse quartz monzonite 37.5%, fine quartz monzonite 25%, Atlanta type granodiorite 12.5%, Cascade type granodiorite 11.0%, and tonalite 9.0% (Larsen, 1958). The Idaho Batholith is surrounded by older rocks on the north, east, and west sides, and overlain by Tertiary lavas on the south side. The average metamorphic age is 102 million years (Larsen, 1954).

The mode of formation of the Idaho Batholith is open to considerable controversy. Anderson (1952) argues for two phases of

emplacement with the earlier phase near the end of the Jurassic and the later phase late Cretaceous. These intrusions were followed by metasomatism. Schmidt (1957) prefers a primarily metamorphic or metasomatic process, with or without mobilization of the interior portion. It is clear that the margins are metamorphosed and/or metasomatised where exposed. Some small portions, especially late or satellitic bodies, are clearly igneous.

One of the most comprehensive reviews of the geology of the Idaho Batholith is found in Swanberg (1973). Swanberg divides the batholith into four groups on geologic and heat-flow criteria.

The west border group of stocks represents about 3% of the total area and is found in the north west corner. It is 105-130 million years old and was emplaced at a depth of 14-22 km. The stocks consist of gabbro, quartz diorite, or tonalite and may be more closely associated with similar late Jurassic rocks in eastern Oregon than with the Idaho Batholith. This group is low in potassium, uranium, and thorium compared with the rest of the batholith.

The main group represents 75% of the batholith. It consists of seven major petrographic units which elongate north to south and grade into each other east to west. The units probably extend the length of the batholith although discontinuously in some cases. This group formed as a unit and is thought to be metamorphic (Swanberg, 1973). It has intermediate potassium, uranium and thorium, and was granitized at a depth of 9-15 km. This group may be offset 150 km east to west along the Salmon River by a fault. The major rock types are gneisses, quartz monzonites, quartz diorites, granodiorites, and migmatites.

Six to seven percent of the batholith is placed in the intermediate group. It consists of 10 major plutonic units which may represent late main stage activity, early Tertiary activity, or a separate event. Ages range from 55 to 77 million years. Emplacement depth was 6-11 km. Chemically this group is similar to the main group. Most of the units are small plutons of quartz monzonite, quartz diorite, granodiorite, or diorite.

The Tertiary epizonal group of plutons represents about 15% of the batholith and consists of over 20 units. It has the highest potassium, uranium, and thorium and was emplaced at 0-6 km about 44 million years ago. It is found mainly on the north, east, and south borders of the batholith. The largest of the 20 units, the Atlanta granodiorite (East), may be a batholith itself. The rocks are mainly granodiorite with lesser granite, quartz diorite, quartz monzonite or microgranite. These shallow intrusives are enriched in potassium but more so in uranium and thorium.

The parameter used in dividing the four groups was non-potassium heat flow over potassium concentration (Swanberg, 1973). This parameter is uniform within a given pluton (or metamorphic unit) but varies predictably between plutons emplaced or granitized at different depths.

The relationship of the Idaho Batholith to adjacent ores has been most thoroughly investigated by Anderson (1942, 1951, 1952). His conclusion is that the Idaho Batholith has no <u>direct</u> connection to any metal deposits. "Such ore deposits as do occur in or near the Idaho Batholith appear to be related to intrusive dikes and stocks that are much younger than the batholith and emplaced under very different

conditions." Anderson believes that the granitized materials from which the batholith formed were deficient in metals. It may be more likely that some phase of the concentration process was deficient, as most sedimentary materials have adequate concentrations of metal to form ores if other conditions are met.

Because of their major economic significance, the silver-lead-zinc deposits of the Coeur d'Alene district deserve consideration. Although the cross-cutting is complex, and the ores remobilized, the vein deposits are generally considered to be late Cretaceous (Fryklund, 1964; Ramalingaswamy, 1975). Nearby intrusive bodies (the Gem Stocks) are petrographically distinct from the Idaho Batholith but are believed to be related (Fryklund, 1964). The time of emplacement of the Gem Stocks was essentially contemporaneous with the emplacement of the Idaho Batholith, about 50 miles away (Fryklund, 1964). The ore deposits are strongly localized by the major east-west trend of the Osburn Fault (Fryklund, 1964).

Important evidence regarding the origin of the Coeur d'Alene deposits is derived from studies of lead isotope ratios. These indicate that the lead present in the Coeur d'Alene deposits separated from sources of radiogenic lead about 1.4 billion years ago (Zartman, 1971; Long, 1960). This is also the age of the Belt Supergroup metasediments (Kanasewich, 1968) which comprise the material from which the Idaho Batholith might have been formed (Schmidt, 1957; Swanberg, 1973). Kanasewich (1968) suggests that the lead in the Coeur d'Alene district as well as that in other lead-zinc deposits related to the Belt Super-

group sediments was originally deposited under conditions similar to those prevailing in the hot brine areas of the modern Red Sea. Geophysical methods detected a Precambrian rift valley below flat-lying sediments (Kanasewich, 1968). The lead in the sediments concentrated about the time the Idaho Batholith was emplaced (Fryklund, 1964) or a little later. Although the source of the lead is unrelated to the Idaho Batholith, the formation of the batholith may still be responsible for the remobilization and localization of the lead into the Coeur d'Alene deposits.

The most probable mechanism for remobilization of the lead involves dissolution in and precipitation from hot chloride-rich brines. A deep unit such as the Idaho Batholith or its satellites near the Coeur d'Alene district may have released these chloride-rich brines (Goodspeed, 1952; Holland, 1972).

Most of the smaller ore deposits near the Idaho Batholith are associated with small early to late Tertiary intrusives, some of which may be unassociated genetically with the batholith. Some of these may be part of Swanberg's Tertiary epizonal group. The fluids released by these smaller intrusives (Holland, 1972) may very well be contaminated by material released from the older batholithic rocks by the later intrusion. The Tertiary intrusive could be contamination by groundwater containing dissolved solids (Kadik, 1965) or by assimilation or stoping of older rock into the Tertiary magma (Kadik, 1966). The first type of contamination has been given an experimental basis for sedimentary rocks (Walker, 1969). Szadeczky-Kardoss (1965) states

". . . intense selective migration of the volatiles takes place even in solid samples at 550°C, in some rock associations already at 250°C, if there is a concentration gradient" and ". . . a high grade contamination of the ascending magma is possible." Once fluids have been released from an intrusive, they may mix with groundwater or leach material from the wall rocks (Ellis, 1967). An intrusive in a chlorine-rich portion of the batholith is more likely to be contaminated by chlorine and is thus more likely to have ore potential.

There is reason to believe that original chloride from the Idaho Batholith or its satellites was not significantly responsible for the Coeur d'Alene deposits. Hietanen (1969) found 100-300 ppm chlorine in schists between Coeur d'Alene and the Idaho Batholith. Scapolite is a common chlorine-containing mineral in the same area (Heitanen, 1967). Heitanen believes that the chlorine is derived from sedimentary halite and is related to the Precambrian rift valley, not the Idaho Batholith. Intrusions related to the Idaho Batholith could pick up chlorine from these schists through mass or fluid assimilation. The increased chloride available for ore transport would most likely be of sedimentary origin.

It is possible that the main connections between the Idaho Batholith and the Coeur d'Alene deposits are thermal and mechanical but not chemical. If the source of material for the Idaho Batholith is a group of sediments which are part of or related to the Belt Supergroup, chlorine-rich sediments could produce chlorine-rich metamorphic and igneous rocks with increased ore deposit potential.

III. ANALYTICAL METHODS

The lack of an ideal method for the analysis of chlorine in rock samples is best illustrated by the large number of methods reported in the literature. It is probably this lack of a good technique which is responsible for the relative scarcity of reports on the amount of chlorine in rocks. The basic requirements for an analytical method for chlorine, from the point of view of this thesis, are a range of 50-5000 ppm, fair to good accuracy, freedom from interference by other rock-forming elements, and reasonable speed per sample, at least with a large number of samples.

Once the sample has been put in aqueous solution, there are several suitable methods. Precipitation of the chloride with excess silver nitrate and measurement of the unprecipitated silver ions with atomic absorption spectrometry is very practical (Belcher, 1972; Reichel, 1969; Truscott, 1970; Westerland-Helmerson, 1966). Although these examples did not use rocks, the method could be easily adapted.

Several methods use electrolytically generated silver ions to precipitate the chloride. The chloride concentration is determined from the amount of solution and the voltage and current versus time curves (Blaedel, 1952; Marinenko, 1963; Masten, 1954; Peters, 1969; Shiner, 1956; Stern, 1958). Mercury electrodes may be used similarly (DeFord, 1956; Przybylowicz, 1956).

Various electrically monitored titrations involving silver nitrate are relatively less convenient, especially on a large scale (Laitinen, 1946; Mokady, 1968). Another group of methods includes colorimetry and

photometry (Kolthoff, 1951; Kuroda, 1950; Menis, 1957; Peck, 1959; Rodabaugh, 1972; Siggia, 1947).

By far the simplest method, once the chloride is in solution, is the use of ion-selective electrodes. A special electrode and a reference electrode are placed in the test solution and the voltage between the electrodes is read. Solutions of known chloride concentration are used to calibrate the voltage. The method is accurate, cheap, simple, and fast (Bazelle, 1971; Black, 1960; Buchanan, 1968; Chanin, 1954; Clarke, 1950; Coetzee, 1969; Haynes, 1972; James, 1972; Mascini, 1969; Mattock, 1962; Rechnies, 1966; Van Loon, 1968, 1971). The method has been applied to Portland cement (Berman, 1972) and rock (Haynes, 1972). Haynes used a method involving fusion of the samples in glass tubes which gave an uncertainty of 120 ppm. There are a number of very similar methods using more standard electrodes (Brown, 1933; Furman, 1935).

The major disadvantage to all of the above methods is the necessity to put the sample into solution. Many fusion procedures call for platinum crucibles. If a multi-sample fusion technique using some sort of inexpensive iron or nickel crucible could be developed, perhaps one of the above methods would be superior. Other problems to be considered with fusion or dissolution are contamination or loss of chlorine through volatilization. The same considerations hold for dissolution by hydrofluoric acid in Teflon bombs. A minor disadvantage of the dissolution methods is that they are all destructive.

There are several potential methods for chlorine analysis which do not involve dissolution or destruction (in the chemical sense) of the sample. The electron microprobe technique is attractive (Leelanandam, 1969) but was unavailable.

Neutron activation is a very convenient method for non-destructive analysis of rocks for chlorine as well as many other elements, if chemical separations are not required. Several published methods (Allen, 1970; Brunfelt, 1971; Gillberg, 1964; Johansen, 1967; Reed, 1966; Reed, 1969; Tajma, 1971; Von Gunten, 1965; Walters, 1971) involve chemical separations, usually after irradiation. These methods are even less convenient than those mentioned previously and would only be considered for small or rare samples or ones with very low chlorine or where contamination is a major risk.

The reason for the chemical separation is that in rocks with normal amounts of sodium (2-4%), the Compton background noise from sodium masks the weak chlorine peak. If the chlorine peak is raised by more intense activation, the radiation from the sodium becomes intense enough to saturate the gamma-ray spectrometer. The radiation from manganese also contributes to the saturation. The sodium and manganese are often removed by chemical means, either before or after irradiation. If they are removed after irradiation, the problem of contamination is avoided, but it is necessary to work with an intensely radioactive sample. Rocks with low sodium, such as coal (Gluskoter, 1970) can easily be analyzed for chlorine in the hundreds of parts per million range we are interested in without any chemical separation.

The advantages of x-ray fluorescence analysis include minimal sample preparation, repeatability, speed, and chemical non-destructiveness. It can be used to simultaneously determine all of the major rock-forming elements and many of the minor elements. There were two reasons why other elements were not determined for this thesis. First, only a limited amount of machine time was available. Second, there is no reason to suspect that the data available from a major element analysis would provide any insight on the processes involving chlorine and ore formation.

X-ray fluorescence has seldom been used for the analysis of rocks for chlorine. Its primary disadvantage is the error due to variations in the effective density of samples with differing mineral compositions and chemistry (matrix effect). This could be eliminated by measuring the mass absorption coefficient but this would sacrifice speed. The increased accuracy is not important for this type of geochemical reconnaissance.

In some cases it might not even be necessary to grind up the rock. A thin section might be used as a sample (Adler, 1966) if it is not too heterogeneous. Using x-ray fluorescence analysis for chlorine would, of course, be especially easy if some related project required major element analyses of the same samples, as these could be done at the same time.

Machacek (1968) analyzed 11 alkalic rocks for chlorine using x-ray fluorescence and spiked standards. His reproduceability was $\pm$ 6.3% at 110 ppm and $\pm$ 3.5% at 300 ppm. Garska (1968) analyzed microgram

amounts of pure silver chloride by x-ray fluorescence. The method is not fully comparable as there was no rock matrix to interfere.

Rucklidge (1972) and Leelandam (1969) used electron microprobes to analyze for chlorine in rock. The microprobe differs from x-ray fluorescence only in its ability to analyze at a point and in the source of excitation energy.

EXPERIMENTAL

I. SAMPLING AND SAMPLE PREPARATION

Representative samples were taken at 74 locations within or near the Idaho Batholith as shown on Figure 1. The samples were collected at about five mile intervals along roads. The samples are described in Table I. Locations were chosen mostly on the basis of accessibility while still obtaining a diversified suite of samples. In some cases the best available sample was still partly weathered.

Petrographic (thin section) studies were not done for this thesis. The information available from thin section work does not correlate well with ore provinces or broad geochemical trends related to ore. DeGeoffroy (1972) finds porphyry copper-molybdenum deposits associated with quartz diorites, quartz monzonites, granites, alaskites, diorites, syenites, monzonites, and porphyritic granites.

Samples were first crushed in a chipmunk crusher. A portion of some of the crushed samples was further crushed, and the 35-80 mesh portion was saved for magnetic separation. The remainder of the samples was pulverized in an alumina ceramic faced mill. After pulverization, the samples were ground for 20 minutes by a motor-driven agate mortar and pestle. Some sample portions were also ground for 10, 15, 30 or 50 minutes to determine any effects of the amount of grinding on the leachability of chlorine.

TABLE I

SAMPLE DESCRIPTIONS

Sample	Schistosity	Color	Biotite	Weathering	Unit	Rock Name	Other Minerals
1	M?	WX	Sm	Sl	Mzi (1)	-	
2	M	VDG	-	N	Tc	Basalt	
3	S	B	*	N	Mzi (1)	-	
4	Sl	OW	*	Sl	"	-	
5	M	LG	Tr	VSl	"	-	
6	M	LG	-	*	Tc	Basalt	
7	M	Bl	-	N	"	"	
8	M	VDG	-	Sl	"	"	
9	M	LG	-	Sl	-	Shale	
10	M	OW	*	Sl	Mzi (2)	"	K, Musc.
11	M	OWF	*	Sl	"	"	" "
12	Sl	W	-	Sl	pC	"	Musc
13	S	G	*	N	-	Basalt	
14	M	DG	-	N	Kpqm	QM	Musc
15	Sl	G	*	Sl	"	"	"
16	S	GF	*	*	"	"	
17	Sl	W	*	N	"	"	
18	S	G	*	N	"	"	
19	M	SlYG	*	N	KTlt?	"	
20	Sl	GP	*	N	KTcc	Microgran	K
21	M	GW	*	N	KTlt	QM	
22	M	OW	*	Sl	"	"	
23	M	OW	*	Sl	"	"	
24	Sl	GP	*	N	"	"	K
25	Sl	LB	*	VSl	-	Pegmatite	K
26	M	YW	Tr	VSl	Kmgm	QM	Musc
27	M	W	Sm	N	"	"	

TABLE I (Continued)

Sample	Schistosity	Color	Biotite	Weathering	Unit	Rock Name	Other Minerals
28	M	VLG	Sm	N	Kmgm	QM	Musc
29	S	DGF	*	Sl	"	"	
30	M	LG	Tr	N	Tvza	-	Epi.
31	Sl	LG	-	N	Tvza	-	Epi.
32	M	LG-G	-	N	"	-	Epi.
33	S	DG-G	-	N	MPzv	Talc Schist	
34	S	DG-GF	-	N	"	Phyllite	
35	Sl	DG	*	N	"	-	
36	S	DG	-	Sl	"	-	Epi.
37	S	DG	*	N	Kqdg	QD	Hb?
38	M	DG	*	N	"	"	
39	M	DG	*	V	"	Tonalite	K, Hb?
40	S	VDG	*	Sl	"	"	
41	M	W	*	V	Kgf?	QM	
42	M	VLG	*	*	"	"	
43	M	VLG	*	N	"	"	
44	M	OWF	*	*	"	"	Musc
45	M	W	*	N	"	"	
46	M	YG	Sm	Sl	"	"	
47	M?	YGF	Sm	N	Kgf?	QM	Musc.
48	M	SlY	Sm	N	"	"	"
49	M	WYG	*	V	"	"	
50	M	OW	*	*	"	"	
51	M	WY	Sm	*	"	"	
52	Sl	Y	*	Sl	"	"	
53	M	OW	Tr	Sl	Kbv	"	
54	M	G	Tr	Sl	"	"	
55	Sl	W	*	N	"	"	K, Hb?
57	M	SlY	*	Sl	"	"	

TABLE I (Continued)

Sample	Schistosity	Color	Biotite	Weathering	Unit	Rock Name	Other Minerals
58	M	W	Sm	N	Kbv	QM	
59	M	GW	Sm	Sl	"	"	
60	M	W	*	N	"	"	
61	M	W	Tr	VSl	"	"	
62	M	VLG	*	N	"	"	
63	M	SlYF	Tr	*	"	"	
64	M	WY	Sm	*	"	"	
65	M	WYF	*	V	"	"	
66	M	WY	*	N	"	"	
67	M	SlYG	Sm	Sl	"	"	
68	M	GY	Sm	Sl	"	"	
69	M	SlY	*	Sl	"	"	
70	M	OW	*	Sl	"	"	
71	M	W	*	Sl	"	"	
72	M	W	Sm	VSl	"	"	
73	M	W	*	N	"	"	
74	M	LY	Sm	V	Ktaw	GD	
75B	M	W	Tr	N	"	GD	

M	Massive	Bl	Black	QM	Quartz Monzonite
S	Schistose	P	Pink	QD	Quartz Diorite
Sl	Slightly	GD	Granodiorite	KT_{lt}	Lolo Trail. QM
V	Very	MP_{zv}	Pre-batholithic metamorphic	Kmgm	Warm Lk. Musc. QM
D	Dark	Tv_{za}	Payette volcanics	KT_{cc}	Cayuse Ck Microgranite
L	Light	F	Ivon Oxide stains	Kqdg	Donnelly QD Gneiss
G	Gray	X	Weathers yellow	K_{bv}	Bear Vy QM
W	White	*	Yes	KT_{aw}	Atlanta GD (West)
O	Off	Sm	Small amount	Kgf	Gold Fork QM & GD
Gr	Green	Tr	Trace		
Y	Yellow	K	K Feldspar		
B	Brown	N	Not visible		

The magnetic separation was done with a Franz Isodynamic Separator. The best settings were found to be: Slope - 30°, Tilt (back) - 15°, Current - 1 amp., Feed - "slow," Vibrator - "8." The two portions resulting from the first pass were separately run through again. The two intermediate portions were combined. The resulting fractions were: a mixture of quartz and feldspars with usually under one-fourth percent mafic minerals, a mafic portion (predominately biotite, usually over 95% pure) and an intermediate portion consisting mainly of grains containing both biotite and quartz or feldspar. Most of the muscovite, when present, was found in this portion. The biotite contents of the rocks are given in Table II. All biotites except sample 16 were from within the batholith. Some of the biotite and quartz-feldspar separates were analyzed for chlorine to determine how the chlorine was partitioned between the minerals. A number of samples were leached in cold distilled water for several days to determine the degree of chloride leachability.

II. NEUTRON ACTIVATION

Several experimental neutron activation runs were made on biotites from the Idaho Batholith (Table III and Appendix B). It was not possible to activate the chlorine sufficiently without saturating the instrument with excess sodium radiation. Calculations indicate that the chlorine peaks were about 50-100 counts in 4-8 channels masked by a Compton noise background averaging 100 counts per channel. Expected standard deviations would be 30-50%. The 2.15 MeV chlorine

TABLE II

MINERAL SEPARATION--PERCENT MICAS

Sample	Biotite in Quartz - Feldspar Fraction	Biotite in Intermediate Fraction	Biotite in Mafic Fraction	Biotite in Whole Rock	Muscovite in Intermediate Fraction
1	-	10	95 +	2.5	-
3	.1	15	95	9.5	-
4	1	10-15	95 +	13.5	-
10	.25	10	95	6.7	1.1
11	.25	10	95	10.9	.8
16C	.5	10-15	95	37.8	.8
F	.25	10-15	95	28.2	-
20	.5	98*	95 +	8.4	-
21	.25	10	95 +	15.3	-
22	.25	30	95 +	6.4	-
24	.25	6	93	5.4	-
26	.25	4	93	2.0	2.0
28	.5	2	50	2.6	2.2
38	.25	15	98 +	11.5	-
40	1	7-10	90 +	28.7	-
45	-	3-5	95 +	4.2	.2
46	1	10	98 +	4.8	-
48	.1	10	59	1.6	.2
52	-	5	95 +	3.4	-
56	-	15*	90*	-	-
57C	.25	15	95	13.6	-
F	.25	15	95	7.0	-
60	.5	65*	95	9.5	-
62	.25	5	95 +	7.2	-
66	-	5	98 +	4.7	-
70	.25	4	90 +	5.3	-

*Indicates mafic mineral other than biotite.

TABLE III

NEUTRON ACTIVATION OF BIOTITES

Sample Number	Weight (gm.)	Neutron Dose (cm^{-2} x 10^{12})	Delay (sec.)	Count Time (sec.)	Dead Time (%)	Correct Count Time (sec.)	Time Efficiency (%)	Dose Factor vs. Standard	Net Peak (2.167 MeV)	Theoretical Pk (cts)
21	2.357	1.3	1266	667	19	600	13	1	-	63
57	.276	17.8	1196	584	28	480	10	13.7	-	109
66	.647	5.5	1302	561	25	480	11	4.23	-	58
16	.260	18.0	869	571	27	480	14	13.8	-	79
LiCl (Standard)	.0638	1.3	156	492	10	480	13	1	3451	-

Peak half height width - 5 channels

Background height - 100 counts/channel

Peaks are equivalent to 1.8 to 3.3 standard deviations.
This would give average errors of 30 to 50% (one deviation).

Reactor run at 5 kw (= 10^{11} neutrons cm^{-2} sec^{-1}).

peak is better than the 1.60 MeV peak because it avoids the Compton background noise from manganese.

The Ge (Li) detector used had an efficiency of 3.5% and a peak to Compton ratio of 12 to 1. Improved detectors have efficiencies of up to 44.9% (Ortec ad, 1974) and peak to Compton ratios of up to 46 to 1 (Harshaw ad, 1974).

III. X-RAY FLUORESCENCE

The sample pellets for the x-ray fluorescence spectrometer were formed by carefully placing about a gram of sample uniformly over a few grams of powdered bakelite in a die and compressing at 20,000 psi by means of a hydraulic jack. The bakelite acts only to hold the rock powder in place as the x-rays do not penetrate beyond the rock layer. Unfortunately, some of the samples were too rich in quartz or feldspar to bind properly. These samples were mixed 6:1 by weight with bakelite and compressed to 10,000 psi. In addition, a heating jacket around the die was used. The drawbacks of this method are longer sample preparation time and interference from the bakelite. The temperature was not high enough to volatilize salt. The interference can be corrected for to a certain extent but the amount of error is substantially increased.

Table IV lists conditions used on the Philips-Norelco X-Ray Spectrograph. It is possible that a silicon or especially a germanium crystal might eliminate much of the interference from the bakelite used to hold some samples together. A germanium analyzing crystal eliminates second order peaks resulting from the chrome x-ray tube

TABLE IV

X-RAY FLUORESCENCE CONDITIONS

Tube	Cr (Mo inferior, Au or Pt possible)
V	45kV
I	30mA
Linear range	0-10,000 counts per second
Crystal	EDDT (Quartz inferior)
K-alpha angle	64.98° (65°)
Background angle	68°
Collimator	Fine
Vacuum	200 microns or better
Detector	Gas flow proportional counter
Gas	P-10 (90% argon, 10% methane)
Flow	.75 cubic feet per minute
Bias	1850 V.
Plateau	Rock 1840-1910 V. Bakelite 1840-1940 V.
Amplifier gain	Coarse 4 Fine 5
Window	.4 - 2.4 V. (Figure 2)

target (Adler, 1966, p. 72). It was not possible to eliminate the bakelite interference by adjusting the bias voltage. The pulse height discriminator partially rejects bakelite pulses in the range 0 to 1 volt (Figure 2). Pulse height rejection is not used if bakelite is absent. If an x-ray tube other than chrome were used, the bakelite interference would probably be eliminated. The machine held eight pellets per run. One pellet (ID-61 + 2% Cl as NaCl) was left in permanently to correct for drift. Each pellet was counted 10 times at 10 seconds each on both the chlorine peak (65°) and the background (68°). Measured peaks and potential interferences are shown in Figures 3 and 4. Including pump down and loading, a run took about 42 minutes. The peaks and backgrounds were totaled and the background subtracted from the peak. The drift pellets averaged 50,847 cts so they were normalized to 50,000 cts. Each pellet in a run was normalized by the same factor as its corresponding drift pellet. The counting error for each pellet was derived from

$$\text{Error} = \frac{100\sqrt{\text{Peak} + \text{Background}}}{\text{Peak} - \text{Background}}\ \%$$

to give the percent error for one standard deviation.

The theoretical way to correct for the bakelite would be to subtract one-seventh of the bakelite net peak (570) and add one-sixth of the total net peak. Because the mass absorption coefficients and densities of the pellets are not accurately known, this method was not maximally accurate. An empirical correction was made by assuming the true mean of pellets with bakelite was equal to the true mean of pellets

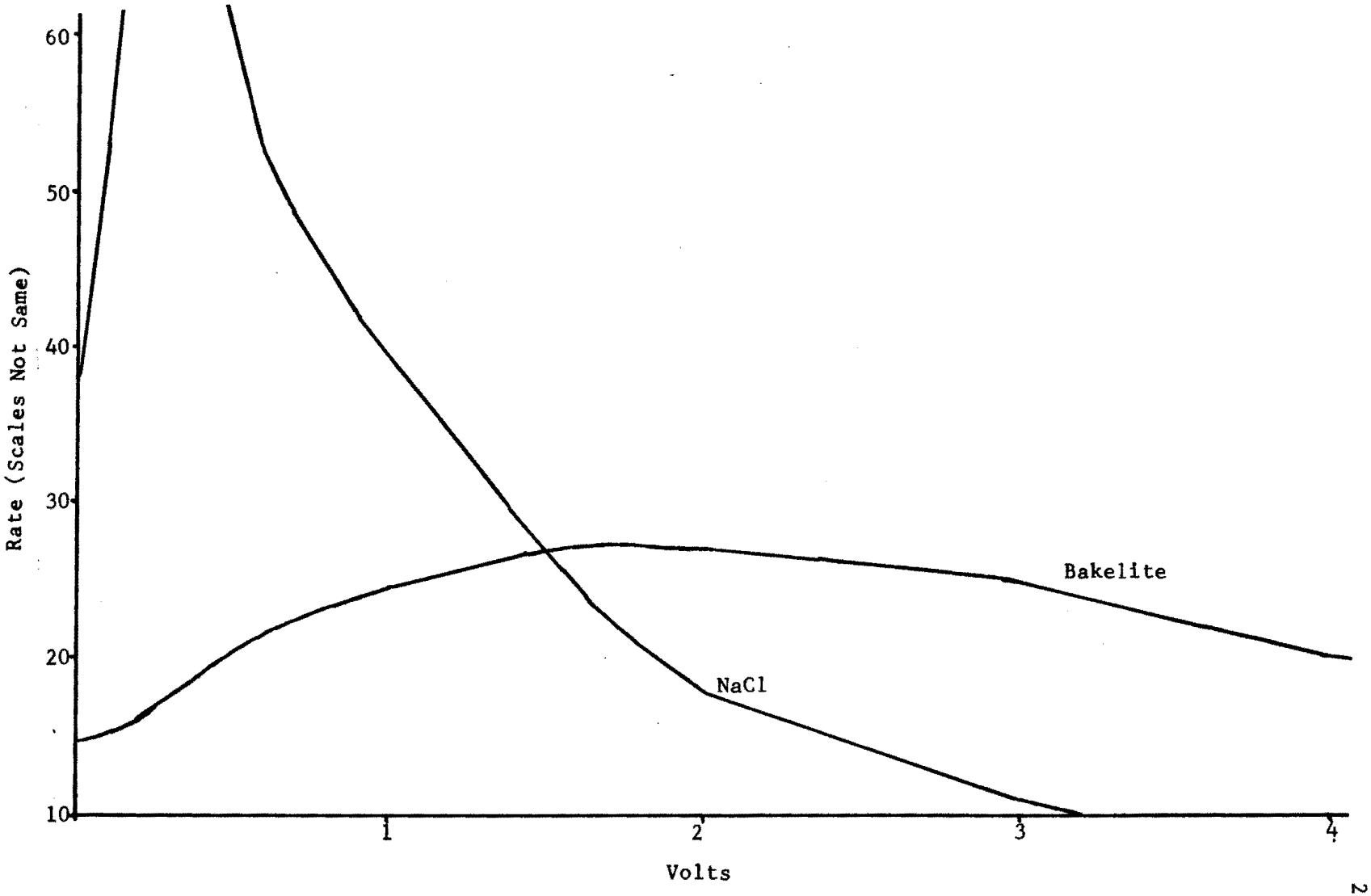

Figure 2. Pulse height distribution.

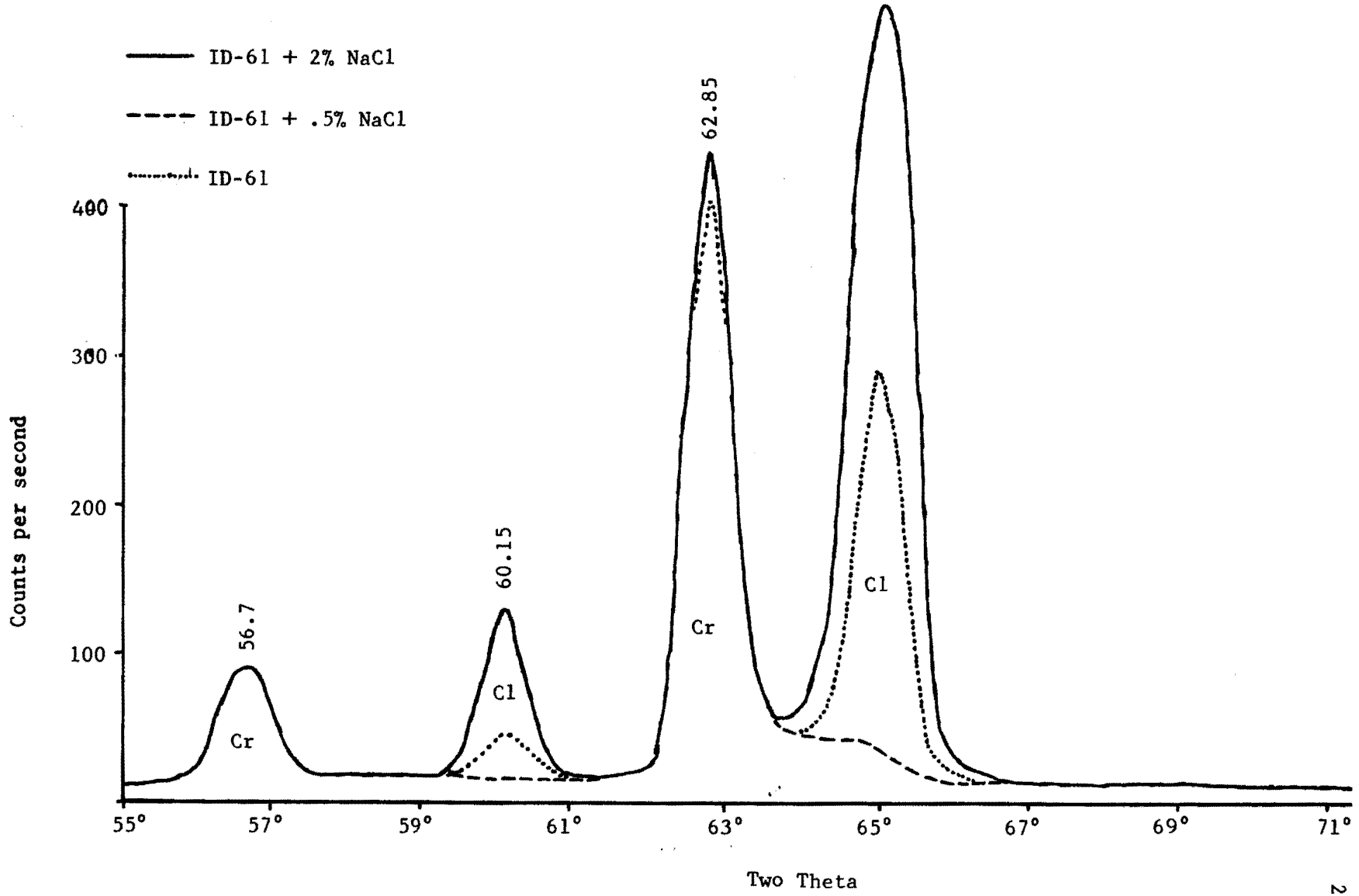

Figure 3. X-ray florescence peaks (Spiked ID-61 scans).

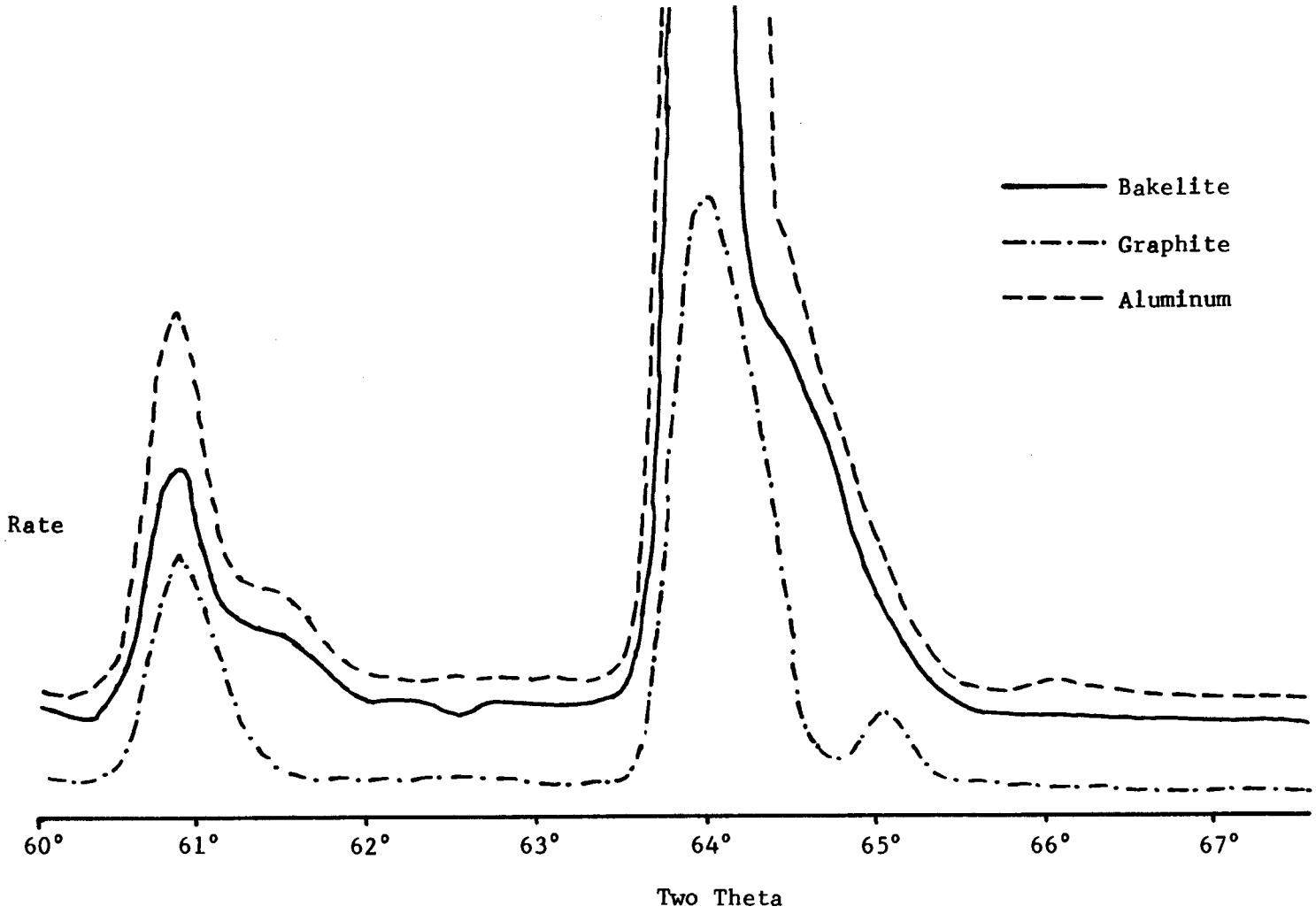

Figure 4. X-ray florescence peaks (Interferences).

without bakelite. This led to subtracting 500 instead of 570 from the peaks of samples with bakelite. Because of the possible errors involved in this type of semi-empirical correction, an additional standard deviation error of 70 cts was assigned to all pellets with bakelite. This may not be as valid for the quartz-feldspar samples.

To convert counts into chlorine concentration, the NaCl spiked samples (sample 61) were graphed as counts/ppm of added Cl and the asymtote determined (Figure 5). The result was 3.0 $\pm$ 2% counts per ppm. Any error here does not affect relative values.

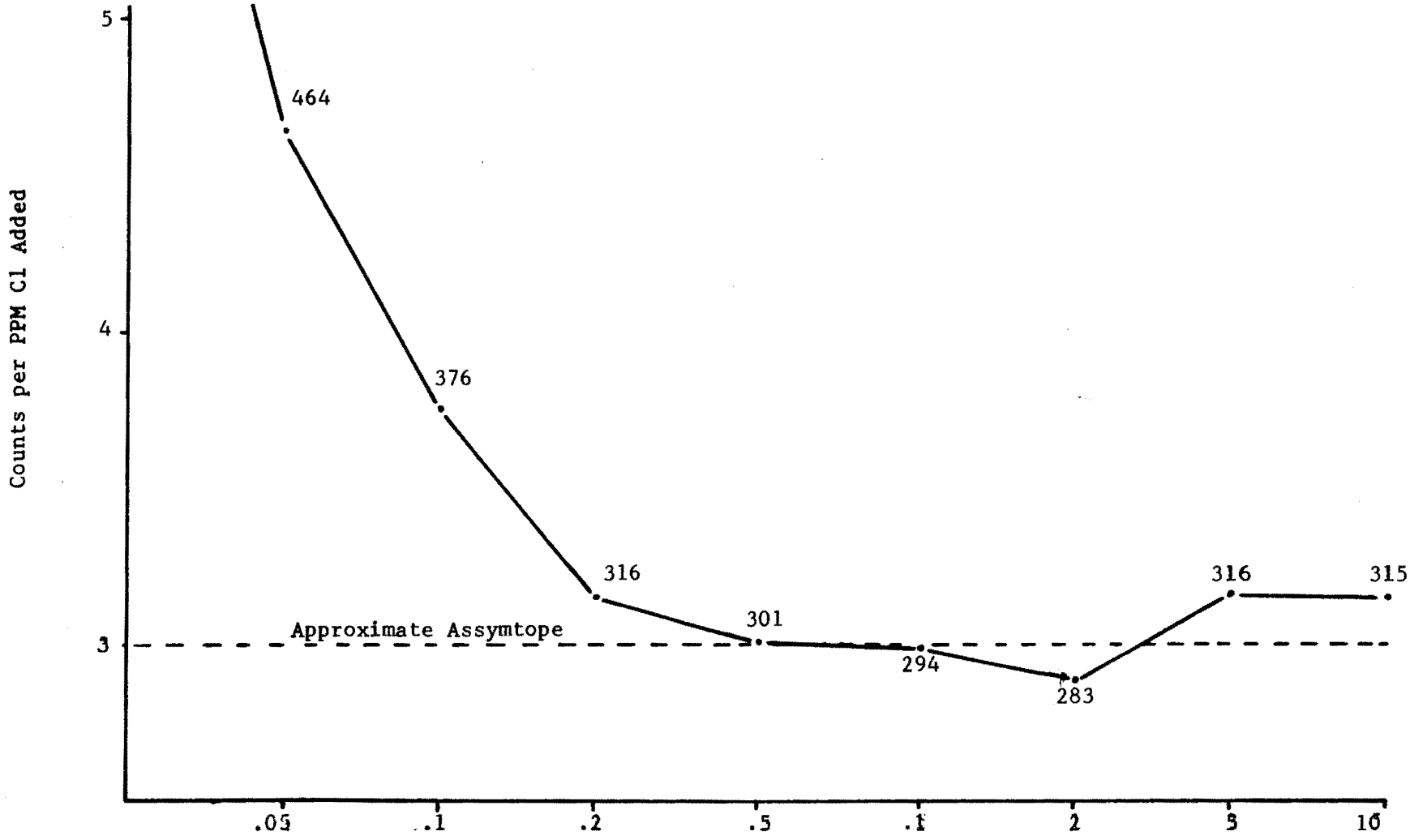

Figure 5. Calibration chart.

RESULTS OF X-RAY FLUORESCENCE ANALYSIS

The full results are listed in Table V and plotted graphically in Figure 6. The mean of all samples was 381 ppm chlorine. Excluding a few high values from the results reduces the mean, the standard deviation, and the standard error of the mean as shown:

Excluding	Mean (ppm)	S.E.M.	Standard Deviation
0	381	4.12%	34.7%
1	369	2.86%	23.9%
2	362	2.24%	18.6%
3	357	1.95%	16.1%
4	355	1.88%	15.4%
5	352	1.85%	15.0%
6	350	1.80%	14.5%

The only samples which differed significantly from the mean were 28, 32, and 45. All were high in chlorine and were from different rock units. These samples may well represent chance variation.

Various rock units were checked for significant deviations (28, 32 and 45 excluded).

TABLE V

RESULTS OF X RAY FLUORESCENCE ANALYSIS

Sample	Net Peak	Sum Peaks	Error %	Sample	Net Peak	Sum Peaks	Error %
1	934	6068	8.3	33	1213	13237	9.5
2	1010	7673	8.7	34	1178	6759	7.0
3				35	1383	4257	4.7
4	1137	5221	6.4	36	1011	9096	9.5
5	880	4908	8.0	37	1507	7642	5.8
6	1155	6528	7.0	38	1086	4596	6.3
7	849	8675	11.0	39	838	5593	8.9
8	799	5838	9.6	40	1269	5756	6.0
9	1508	6207	5.2	41	688	4075	9.3
10	974	4075	6.6	42B	937	4554	14.7
11B	824	3538	15.2	43	767	4914	9.1
12	945	3656	6.4	44	1058	3670	5.7
13	1165	5495	6.4	45B	3729	7478	4.2
14	1129	4188	5.7	46	1189	5488	6.2
15	1094	6380	7.3	47	1065	4683	6.4
16	892	5047	8.0	48B	747	3664	17.5
17	1141	5202	6.2	49	997	4706	6.9
18	991	5283	7.3	50	1160	4556	5.8
19	1180	3344	4.9	51	1090	5816	7.0
20				52	976	5069	7.3
21B	1057	4381	13.3	53B	1191	24859	17.6
22	1167	5293	6.2	54	1201	6038	6.5
23	723	3431	8.1	55B	1015	5632	14.3
24	1180	6056	6.6	56	1296	5659	5.8
25	809	3572	7.4	57	1063	4935	6.6
26B	1322	5836	11.1	58B	1051	5077	13.4
27B	1472	5378	10.1	59	838	4632	8.1
28B	2484	6190	6.0	60	956	3972	6.6
29	1204	6970	6.9	61B	1475	5102	9.6
30	1096	5685	6.9	62	1044	5391	7.0
31	1202	5130	6.0	63			
32B	2086	6220	7.3	64	997	3584	6.0
20 QF 10B	524	4354	26.0	50 FP L50B	776	6900	19.7
" " 20B	602	4491	22.7	62 - 10	1113	5497	6.7
" " 50	1160	4159	5.6	15	1255	5944	6.1
" "L10B	833	4413	16.4	30	824	5383	8.9
" "L20	861	4061	7.4	L10	948	5477	7.8
" "L50B	835	4070	16.0	L15	903	5197	8.0
38 QF 10B	775	4478	17.6	L20	956	5373	7.7
" " 20B	821	4205	16.4	L30B	980	5543	14.7

TABLE V (Continued)

Sample	Net Peak	Sum Peaks	Error %	Sample	Net Peak	Sum Peaks	Error %
38 QF 50	1062	3995	6.0	30B	576	5149	19.4
" "L10	1105	3941	5.7				
" "L20B	801	4168	19.2	66 QF10B	972	4543	14.1
" "L50B	605	3988	26.0	20B	514	4682	21.7
50 FP 10B	495	6425	30.3	50B	831	4681	16.6
" " 10	961	8653	8.6	L10B	763	4546	18.1
" " 50B	758	7235	20.4	L20B	664	4406	20.5
" " 50	829	6574	9.8	50	931	4106	6.9
" "L10B	832	6704	18.2				
" "L20B	804	6625	19.9				
		Biotites					
65	966	4848	7.2	61B + 2	57,750	52,350	0.5
66	1041	4928	6.7	5	158,065	138,396	0.3
67	1055	4734	6.5	10	314,858	273,604	0.2
68B	1102	4259	12.3	BC 0	3989	9363	2.4
69	1149	5578	6.5	BF 0	4107	9436	2.5
70	1168	4864	6.0	NaCl	779,191	798,853	0.1
71B	749	5425	19.1	B + .1	20,070	29,440	0.9
72	1022	4964	6.9	+ 1	36,972	46,315	0.6
73	1025	3245	5.6	+ 10	265,079	276,549	0.2
74B	1165	5675	13.5	45 QFLB 20	704	4674	19.6
50FP	901	6773	9.1	" + .01	873	5066	16.2
50M	1073	6564	7.6	" + .025	1743	5394	8.2
				" + .1	2809	6353	5.3
				" + 1	23,519	26,604	0.7
21	1251	8046	7.2	" + 10	234,065	202,955	0.3
40B	1788	9115	9.2	50 FPLB			
66	973	9123	9.8	+ .01	732	6604	20.7
57C	1255	7598	6.9	+ .025	979	6857	15.5
20	1352	8878	7.0	+ .1	2578	8091	6.2
16F	778	6932	11.0	+ 1	18,896	22,078	1.2
16C	1116	7545	7.8	+ 10	201,144	176,433	0.3
4	1751	9287	5.5				

TABLE V (Continued)

Sample	Net Peak	Sum Peaks	Error %	Sample	Net Peak	Sum Peaks	Error %
	Standards				Other		
61B + .001	811	4833	17.3	1QF	979	5007	7.2
.002	943	4525	14.5	26QF	919	4104	7.0
.005	942	4956	14.8	52QF	991	4517	6.7
.01				74QF	1170	4925	6.0
.02	1447	4709	9.7	45QFB	491	4554	28.0
.05	2329	5798	6.3				
.1	3758	5415	3.9				
.2	6333	9652	2.9				
.5	15,055	15,124	1.4				
1	29,899	30,182	0.8				

LEGEND

First Number - Sample
Second Number - Minutes of Grinding
Plus Number - Percent added chlorine
B - Bakelite added
FP - Feldspar pegmatite
QF - Quartz Feldspar fraction
L - Leached
M - Muscovite
C - Coarse (16-35 mesh)
F - Fine (35-80 mesh)

All corrected for bakelite error $\pm$ 70 counts.

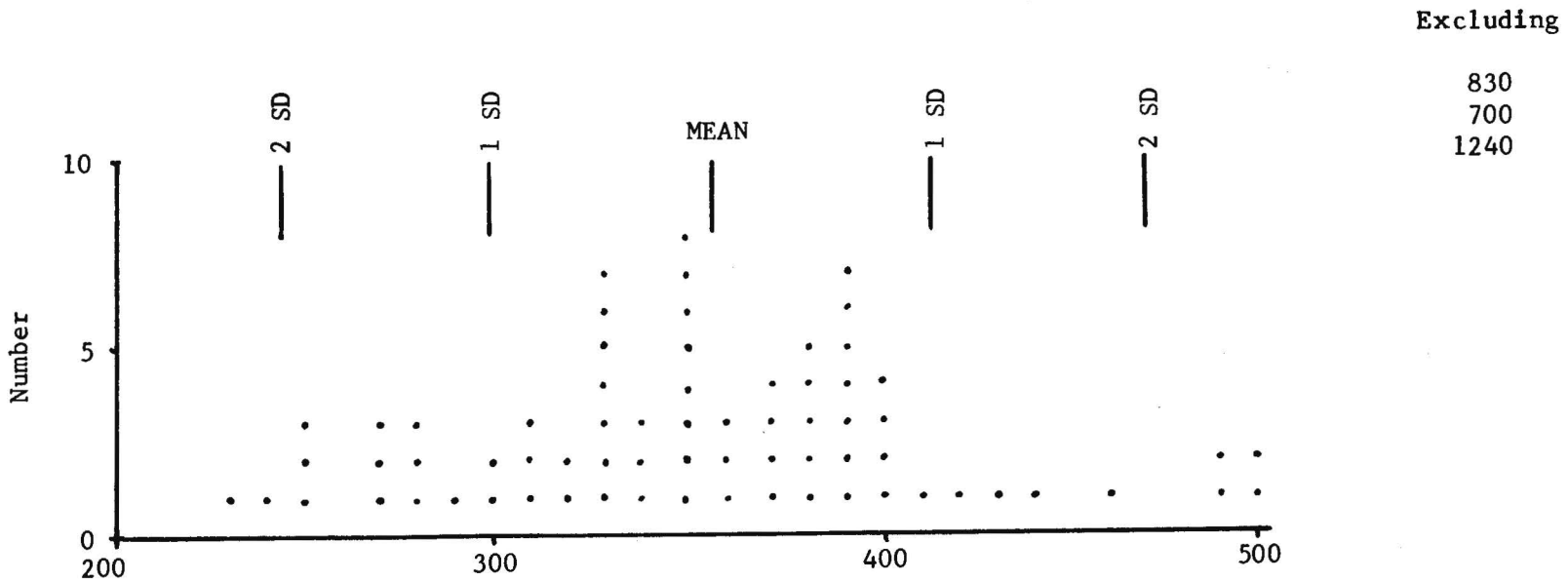

Figure 6. Histogram of chlorine contents.

Group	Age	Mean	Standard Deviation Found	S.E.M. (Calculated)
1-6	Meso.	342 ppm	3.5%	6.4%
8-9	Tert.	384	8.3%	10.9%
12-30	Both	365	3.0%	3.9%
31-36	Cret.	399	11.3%	6.4%
37-40	Cret.	339	4.5%	7.7%
41-56	Cret.	399	11.3%	4.1%
57-74	Tert.	351	1.0%	3.7%

Only group 41-56 had a mean significantly different from the overall mean at the 95% confidence level. It had a mean 3.2% over the 95% level. This is statistically significant but not important as a guide to ore provinces. Neither age, geographic location, nor rock composition had geologically significant variations in chlorine.

The means of 12 leached and 15 unleached samples were 270 ppm and 263 ppm. The SEM is 4% so this difference is insignificant.

Nine samples each of 10, 20, and 50 minutes of grinding gave average values of 543 ppm, 484 ppm, and 572 ppm respectively. The SEM of each is 5.1% so the differences are not significant.

A histogram of counting errors is given in Figure 7. If it assumed that the regional distribution (over five mile spacing) is completely uniform, the standard deviation due to sampling error is the overall standard deviation (16.1%) minus the mean counting error (8.2% approximately), or 7.9%. Thus the maximum possible sampling error is less than the counting error. The actual sampling error depends on the

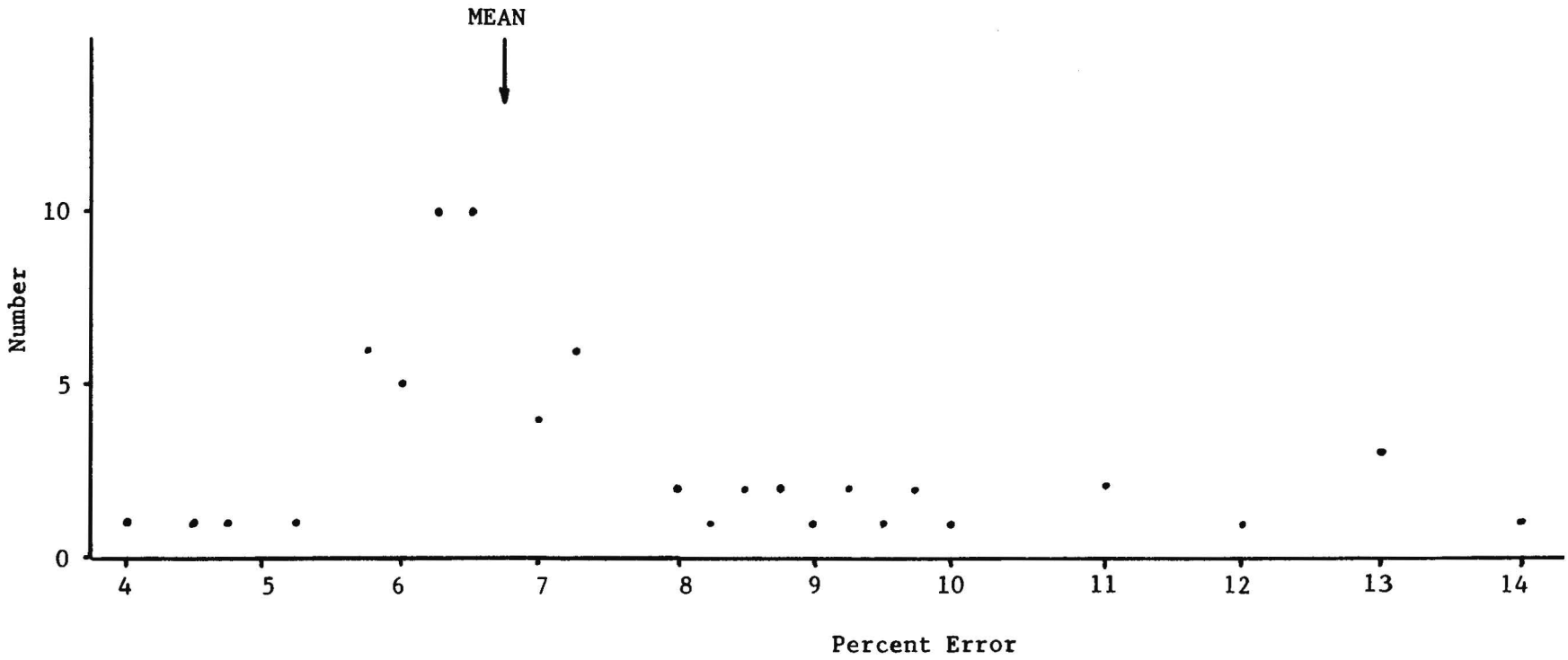

Figure 7. Histogram of counting errors (One standard deviation).

scale and amount of variability which is not known. It is not significant for the purpose of this thesis. The sampling error could be reduced by a factor of the square root of the proportion of additional samples taken if the sample spacing is greater than the interval of variability. Likewise the counting error could be reduced by a factor of the square root of (the number of seconds counted/100).

It is possible that the distribution of chlorine values is somewhat lognormal rather than normal (Rodionov, 1965), but not enough samples were analyzed to verify this. This would make the significance of samples 28, 32, and 45 somewhat less since high values are more frequent with lognormal distributions than with normal distributions.

The biotite and quartz-feldspar fractions from the Idaho Batholith have approximately equal chlorine. The apparent weathering, as indicated by ease of sample crushing, had no significant effect on chlorine content. The samples within and without the batholith have similar values for chlorine. The degree of metamorphism showed no correlation with chlorine content.

DISCUSSION

Chlorine is nearly uniformly distributed over the sampled part of the Idaho Batholith and the average concentration was about 380 ppm. This tends to support the metamorphic hypothesis for the origin of the Idaho Batholith. If the Idaho Batholith is composed of multiple igneous intrusions, chlorine must have fractionated nearly equally in most of them. Although this is possible, it is not too likely. We would expect different intrusions of varying age composition, and history to contain different amounts of chlorine. Differences in chlorine contents between adjacent sedimentary layers would be relatively easy to homogenize through metamorphism as opposed to separate intrusives which could be up to 200 miles apart. Cretaceous and possibly Tertiary thermal events could have homogenized the chlorine. Due to the wide variation of chlorine in sedimentary rocks, it is unlikely that the chlorine was uniform before strong metamorphism occurred.

The lack of correlation of chlorine concentration with metamorphic grade is probably due to lack of medium grade metamorphic samples. Along the west side at least, the batholith is probably in fault contact with much less metamorphosed rock. The rock outside the batholith was not metamorphosed enough to drive off chloride. The large size of the batholith might make a nearly closed system with respect to chlorine, especially in the area sampled which was nearly all of the very high metamorphic grade. The zones of moderate metamorphism where chlorine

loss might be expected to be high was not sampled. Chlorine saturation was not reached as similar rocks have shown much higher amounts of chlorine. Chlorine was derived from a rather uniform and therefore probably sedimentary (Beltian) source. Fracture controlled loss of chlorine during metamorphism did not appear to upset this uniformity in any major region sampled. The Tertiary epizonal material may be derived from a similar source or may have equilibrated, at least with respect to chlorine, with the metamorphic material.

The overall indication is one of either little or uniform chloride escape which fits with the scarcity of Cretaceous ore within the batholith proper. Chlorine would probably tend to escape along major fracture systems. This would leave areas near fracture systems low in chlorine. No broad anomalies either positive or negative were found, however narrow anomalies would have been missed.

Highly metamorphosed rock showed the same chlorine content as nearly unmetamorphosed rocks, arguing for little loss in chloride. Early loss of chlorine would have resulted in lower overall levels of chloride as metamorphism progressed. It is reasonable to assume the chlorine in the original sediments was broadly homogeneous horizontally, as later homogenization on this large a scale is unlikely.

Since chlorine is, now at least, nearly uniform, its relation to the ore transporting problem is ambiguous. It is possible that Noble's ore province (see Appendix A) is partly an artifact of the methods he used to define it. He grouped most known mines and prospects according to their size and proximity. Genetically unrelated deposits which happened to be close to each other were placed in the same province.

If the chlorine was present as strongly saline fluids in large inclusions, it would be expected to be more water or weather leachable than it was. The chlorine is either in very small inclusions or in crystalline solution. Large inclusions would not be favored by slow crystallization or metamorphism. Slow growth fills in convexities before they can be sealed off. Small inclusions are consistent with Swanberg's (1973) interpretation that the main group is metamorphic. Residual water may have remained in solution in the rock through metamorphism. At sufficient depth, the partitioning coefficient of chloride into the aqueous phase may not be as high. In either case, there was probably little available chloride to form ore solutions in the batholith proper in the later part of metamorphism. This, along with erosion, might explain why the batholith proper does not have many associated ore deposits. Later intrusives could rise, form saline solutions, and produce ore fluids. The amount of chlorine or metal contributed by the batholith to the intrusives is unknown. Clearly the largest intrusives did not pick up any appreciable chlorine from the batholith, as there was no apparent leached zone in the older metamorphic rocks.

In any event, since the chlorine appears to be uniform over the batholith proper, somewhat similar amounts could be expected to be contributed to the intrusives. In terms of prospecting, each of the later intrusives must be individually checked.

The approximately equal chlorine concentrations of the quartz-feldspars and the biotites explain the lack of correlation between chlorine content and biotite content. If the chlorine were concentrated

in one mineral, the overall distribution of chlorine in the rocks would be more lognormal than normal (Rodionov, 1965). The distribution found was close to normal.

The Coeur d'Alene deposits have only been remobilized a very short distance, and the source rock was highly mineralized (Ramalingaswamy, 1975). Ample chlorine is available in the surrounding metasediments to transport this ore without calling for a contribution from intrusions (Hietanen, 1967). It would be of special interest to determine the chlorine content of intrusives associated with the Coeur d'Alene deposits as well as the surrounding metasediments. As was mentioned previously, the salinity of hydrothermal fluids is controlled by many more parameters than the chlorine content of the country rock. Consequently, a measure of the chloride content of the hydrothermal fluids would be a better indication of ore potential than the chlorine content of the country rock. A record of the hydrothermal fluids should be preserved as fluid inclusions or impurities in the gangue materials of ore veins. Materials from barren versus ore-bearing veins may very well indicate significant differences in the hydrothermal fluids which formed the vein. Quartz would be the preferential material to study from an experimental viewpoint. Neutron activation analysis would be facilitated by the low sodium in quartz. Additional elements could be simultaneously determined. Zinc, silver or gold, for example, would indicate base metals in the fluid. Aluminum may indicate extent of wall rock alteration and may be related to gold mineralization. Potential exists for autoradiography of neutron activated vein slabs. This would provide a graphic indication of element distribution. If chlorine suffers from interference

from other elements, it might be necessary to use a scanning electron microprobe.

Feldspar or other sodium rich vein materials could be analyzed using any of the whole rock methods mentioned previously, such as ion selective electrodes. Sodium would block the autoradiography of activated chlorine.

It might also be possible to determine the temperature of ore formation from the Ca-K-Na ratios in quartz gangue. These elements can all be analyzed by neutron activation (Yule, 1965).

There is insufficient experimental data to determine the chloride content of hydrothermal fluids from the chlorine contents of the associated whole rock or any of its mineral phases. Study of these relationships could be useful in other aspects of geology. Pressure at the time of mineral formation might be determinable (Kilinc and Burnham, 1972).

A broad geochemical reconnaisance such as this thesis could be used to select small areas for more detailed study. This could be done for the areas around samples 28, 32, and 45, for example.

SUMMARY

1. The Idaho Batholith has a relatively uniform chlorine content of 380 ppm. The distribution is either normal or slightly lognormal.

2. The chlorine in the batholith probably did not influence mineralization trends in the area. Chlorine was probably originally part of sedimentary rocks but has since been remobilized locally by intrusions. Additional work might show small scale trends in or near Tertiary intrusives post dating the batholith.

3. The Coeur d'Alene deposits may be related to the Idaho Batholith mechanically and thermally but probably not chemically.

4. X-ray fluorescence is best used for chlorine analysis when other elements are being analyzed by the same procedure. In other cases ion selective electrodes or neutron activation analysis is a better choice.

5. The possible existence of a base metal province in part of the region studied is not due to variations in chlorine content of the country rock.

6. The chlorine was probably homogenized by Cretaceous metamorphism. The system may have been closed on a regional scale.

7. Most of the chlorine is present in the quartz-feldspar minerals in the form of very fine fluid inclusions. Large inclusions would have been leached out experimentally.

8. The metamorphic or granitization theory is supported, versus the multiple intrusion theory.

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APPENDIX A

REVIEW OF LITERATURE

I. THEORIES OF ORE FORMATION

The problem of the origin of ore deposits has interested geologists for many years. The average crustal abundances of lead and zinc, for example, are only about .05% of the minimum grade required at present for economic recovery. Many ore deposits represent even greater degrees of concentration than .05%. Unlike many geologic processes which result in the dispersion and dilution of elements, the ore-forming processes represent an extraordinary degree of concentration.

All three of the major rock-forming processes, sedimentary, igneous, and metamorphic, can result in those very specialized rocks which are base metal ore deposits. Sedimentary deposition is clearly demonstrated by the Kupferschiefer (Germany), the Katanga copper belt (Zambia), the Northern Rhodesia copper belt, as well as several others (Knight, 1957). In many cases, however, base metal deposits are epigenetic. Krauskopf (1971) has suggested that sedimentary materials enriched in metals could be a very suitable source for further concentration by igneous or metamorphic processes.

Early in the history of geology, a strong correlation was noted between igneous intrusives and ore deposits, especially gold, silver, and the base metal sulfides. For many years it was assumed that the

intrusive was the source of the metals in the ores. In a few instances this has been clearly shown.

Although metamorphism is not as conclusively connected to epigenetic base metal ore deposits as igneous activity, there are many similarities between them. High grade metamorphic processes grade into igneous intrusive processes. In many areas, such as the Idaho Batholith, igneous activity is associated with the metamorphism. Goodspeed (1952) discusses the generalized problems involving mineralization related to granitization. He states:

> All field and petrographic data point definitely to the assumption that the Cornucopia veins have been formed by hydrothermal solutions which were active in the retrogressive stage of the metamorphism following the granitization.

The Cornucopia gold veins are in "an irregular stocklike grandioritic mass" satellitic to the Idaho Batholith. For the purposes of this thesis, it is not necessary to draw much distinction between igneous and metamorphic processes involved in ore formation as chlorine could play nearly the same role in either case.

In igneous and metamorphic processes, four mechanisms exist which might explain the transport of base metals or base metal sulfides. Transport is necessary to concentrate the metal from the diffuse state in which it is found in source rocks. One means of transport is as a magma. With the possible exception of Fe-Ni-Cu sulfide deposits associated with mafic magmas such as at Sudbury, Ontario, the mineralogy and chemistry of ore deposits show no evidence for the presence of a metal sulfide magma as a separate, immiscible phase (Hawley, 1965). Even in the case of Sudbury, other interpretations are possible (Cheney, 1967).

Another means of transport is solid state diffusion (Verhoogen, 1952). This mechanism is too slow and limited in range to be effective. Some transport may occur in the vapor state, especially for volatile metals such as mercury, arsenic, or antimony. The volatilities of gold, silver, lead, zinc, or copper are far too low for this mechanism to work for these elements under 400°C (Krauskopf, 1964). Krauskopf states:

> Volatility, therefore, cannot be a general method of ore-metal transportation, but has possible significance in the separation of metals from magmas and the zones of high-grade metamorphism, and perhaps in the deposition of some high-temperature ores.

The conclusion is that base metals in epigenetic ore deposits must be transported, at least in later stages, primarily as an aqueous solution. This applies to sedimentary, igneous, or metamorphic base metal ores.

It is known experimentally that base metals or their sulfides are nearly insoluble in pure water regardless of the temperature or pH (Czamanske, 1959). When large amounts of chlorides are added, usually as NaCl, the solubilities of the metals increase enormously (Holland, 1972). This is due to chloride complexing (Anderson, 1973). There is experimental evidence for other types of complexing, such as bisulfide, but unlike chloride complexing, these theories are not supported by field observations or ore fluid inclusion studies.

In a few cases, such as the Taupo Volcanic Zone, New Zealand, base metal sulfides have been and are being deposited from very dilute solutions (Weissberg, 1969; Browne, 1969). Maximum metals in solution are 1 ppb Au, 2 ppb Ag, 15 ppb Zn, 12 ppb Cu, 5 ppb Pb (Browne, 1969). Sulfide sulfur is about 120 ppm and chloride is probably about 1200 ppm. Bisulfide or sulfide complexes could easily carry these traces of metals

but so could chloride complexes (Weissberg, 1969). The gold-silver deposits observed would require roughly 800 km^3 of the above solution (Weissberg, 1969). Since a cooling intrusion probably releases only 1-5 weight % water (Holland, 1972), it is likely that most of the ore solution water is meteoric. Examples of deposits of this type are the epithermal disseminated gold deposits at Carlin, Nevada (Weissberg, 1969). The volumes of solution required are too large to explain most epigenetic base metal deposits (Roedder, 1960).

Dense brines are less likely to reach the surface than very dilute ore fluids of the Taupo type (White, 1974), so ore transported by dense brines would not often deposit as near the surface as ore of the Taupo type. This would restrict observation of modern dense brine ore fluids.

Although there is some conflicting data (Anderson, 1973), it appears that sulfide or bisulfide complexes are inadequate to transport lead (Anderson, 1973; Hamann, 1973) or iron (Barnes, 1967). Pyrite is common in hydrothermal vein deposits, indicating that iron is easily transported.

Chloride complexes are much less stable at lower temperatures, and thus cooling of hydrothermal solutions containing metal-chloride complexes can result in the precipitation of metal sulfides if reduced sulfur is present. Neutralization of acidic hydrothermal solutions by reaction with certain wall rock minerals such as calcite or feldspar can also result in deposition, even isothermally (Helgeson, 1970).

The prerequisites for the formation and transport of an ore-bearing fluid are: (1) source of metal, (2) water, (3) heat, (4) chloride source,

(5) driving or transporting force, (6) suitable path through which to move (permeability or fracture). An acidic solution encourages solubility of base metals but may not be vital in ore transport. Combinations of common minerals such as quartz-K feldspar-muscovite can act to buffer aqueous solutions at a pH of 4 to 4.5 at 300°C (Hemley, 1959).

Due to the close spatial and temporal relationships between many hydrothermal base metal deposits and igneous intrusive or metamorphic events, it is often assumed that the igneous intrusion or metamorphic event supplied the metal, chloride, water, heat, force, and path necessary to form an ore-rich fluid and move it to a zone suitable for deposition. This is the Plutonist theory, which holds that slowly crystallizing intrusives give off water, forming an aqueous phase into which chlorides and then metals are partitioned. The intrusion fractures the country rock. The same forces which fracture the country rock force the ore-rich fluids out into the country rock where they can deposit. Cooling cracks or faulting can also serve to release the ore fluids.

Some modern theories of ore formation emphasize that the only element necessary for ore formation, clearly traceable to the intrusive event in every case, is the heat. In the lateral secretion theory, for example, the intrusion supplies heat to ground water which reduces the density of the water. Convection then pulls ground water towards the intrusive at lower levels while the heated brine floats up and away from the intrusive at higher levels. Water, metal, and chloride are all

present in the intruded rock and can be made available by heat and pressure (Ellis, 1967). Taylor (1974) supports the importance of meteoric water in many ore deposits with oxygen and hydrogen isotope data.

If an intrusion is water saturated, it may add water with or without chloride and metal to the groundwater. If the intrusion is undersaturated and fractured, groundwater may enter it and leach chloride and metal, permeability permitting. Water movement depends on the relative activity of water in the intrusive versus the country rock (Kadik, 1965). Depending on conditions, the ore-bearing fluid may deposit as it nears the intrusive, as it passes through the intrusive, or as it cools near the top of the convective cycle.

In composite igneous-metamorphic terrain such as the Idaho Batholith and surrounding area, saline solutions trapped in rock pores may be forced or sweated out by compression. The heat could be supplied by the geothermal gradient or local intrusions. Associated faults can provide a path for the fluids. The fluids are forced to regions of lower pressure. As these fluids migrate, they may leach the wall rock and become increasingly rich in chlorides and metals.

Many modern theories for base metal ore deposition involve a final concentration or mobilization of metals by means of a hot chloride-rich brine. Boyle (1967) believes some ore deposits are locally derived by the leaching of metal from vein wall rock. Knight (1957) summarizes stratigraphic controls on ore deposition (syngenetic theory). White (1968, 1974) classifies a number of hydrothermal systems on the basis of

the origin of the water involved in ore transport: meteoric, oceanic, evolved connate, metamorphic, and magmatic. He states:

> Individual constituents, including the metals, Cl, S, and CO_2, may come from the same or different sources than the dominant water. Igneous intrusions frequently provide the energy and perhaps the S and C of the ore deposits, but a magmatic origin of the metals, H_2O, and other constituents is commonly assumed uncritically.

Lovering (1961) proposes that some ore deposits form by the mixing of two hydrothermal fluids, one metal rich and one sulfide rich. Of the 40 deposits and districts reviewed by White (1974), nine show isotopic or chemical evidence of mixing of two fluids while only two provide evidence that mixing was probably not involved. Krauskopf (1971) argues for a pre-enrichment (two stage process) of the material from which the metal is leached. Metal rich sediments are the source for later epigenetic ores. The degree of pre-enrichment versus probability of ore deposits is not simple or quantified.

Through all these arguments it should be remembered that demonstrating that one model is the most reasonable does not imply that it is the only correct one when many deposits are considered. The absence of any one of the factors necessary for ore fluid formation may prevent the formation of ore deposits in an area or region. At the present state of knowledge, it is very difficult to say which factors are most likely to be limiting in the ore-fluid forming process. It is even possible that some physical aspect of deposition or later erosion is the most limiting factor in the existence of ore bodies.

II. BASE METAL SOURCES

If metal content of the host rock or intrusive was the most common limiting factor in ore-fluid formation, an obvious approach to geochemical prospecting would be to look for regions with anomalously high or low base metal content. Numerous attempts have been made (Blaxland, 1971; Brabec, 1971; Flinter, 1972; Tilling, 1973) to correlate ore districts or provinces with average base metal content of the country rock or intrusives. No correlations were high enough to be predictive. Indeed, it is not even certain whether one should look for ore deposits in positive or negative anomalies. The formation of the ore-bearing fluid reduces, at least locally, the concentration of base metal in the source rock. Perhaps we should look for local negative metal anomalies within positive regional ones. Boyle (1968) lists several negative metal anomalies associated with ore veins from the Yellowknife and Keno Hill (N.W.T., Canada) districts. It is not known how representative these might be. In order to help quantify the concentration processes in ore formation, concentrations of metals available in typical source rocks are given in Table VI. If the extraction efficiency of the aqueous fluids is high enough, these average metal concentrations could easily generate fluids of 1 to 100 ppm metal, the concentrations of base metals thought to be likely in ore depositing fluids (Roedder, 1960). The largest ore deposits associated (spatially and temporally) with the Idaho Batholith are the Coeur d'Alene lead-silver-zinc group. It is now proposed that these deposits were derived from the metamorphosed sediments of the

TABLE VI

AVERAGE METAL CONTENTS OF ROCKS (IN PPM)

	Silver*	Zinc**	Lead***
Shales, Clays, Muds, Graywackes	.1 (.07 - 15)	120	22
Quartz Sandstone	.1? (.1 - 2.6)	34	19
Limestone, Dolomite	.1? (.1 - 20)	23	9
Basalt-Gabbro	.1? (.03 - 7.44)	60 (10 - 120)	6****
Andesite-Diorite	.06? (.05 - .08?)	80 (20 - 130)	15****
Granite-Granodiorite	.05? (.02 - 64.9)	110 (50 - 190)	19****

Ranges of values in parenthesis.

*Boyle, 1968

**Wedepohl, 1969

***Wedepohl, 1971

****Turekian and Wedepohl, 1961

Belt Supergroup (Ramalingaswamy, 1975). Lead isotope data agree with this interpretation (Zartman, 1971).

It is not possible to estimate to what extent high country rock metal concentrations affect the probability of ore deposits in a region. It is known that high country rock metal concentrations are not a common feature of the rock surrounding most ore deposits. The amount of metal mobilized in an ore fluid forming system is the product of the volume of source rock affected, source rock metal concentration, and extraction efficiency.

III. CHLORINE SOURCES

An important assumption of this thesis is that, other things being equal, chloride-rich rocks or magmas will tend to form chloride-rich solutions by leaching or fractionation. The physical and mineralogical distribution of chlorine within rock may have a considerable effect on leaching of chloride. The chlorine in biotite, for example, has a structural location and may thus be resistant to leaching. If chloride is derived by partitioning into the aqueous phase of a cooling intrusive, its distribution within the various minerals of a rock will reflect the varying chloride concentrations during the paragenetic history of that rock. If associated ore deposition could be traced to a particular stage of paragenesis, the minerals formed in this stage would probably have a chloride content which would reflect the ore-forming fluid more accurately than the whole rock chloride content. Thus if ores are derived from late magmatic fluids, then late forming minerals

would provide a better indicator of available chloride than early forming minerals.

Very little is known about the partitioning of chloride between the various coexisting mineral phases. Evans (1969) found tens to 1200 ppm chlorine in coexisting muscovite and biotite in pelitic schist. Biotite had 100-1200 (average 300) ppm and muscovite had tens to 100 ppm. The accuracy was $\pm$ 100 ppm by microprobe analysis. There was no correlation between the chlorine contents of the biotite and muscovite. Gillberg (1964) found no correlation in chlorine contents between coexisting biotites and amphiboles in 34 Swedish granites. Biotite had 100-6,600 ppm chlorine. The range in the whole rock contents was not as wide. It was not stated whether all the biotite was primary. Kuroda and Sandell (1953) give 50-580 ppm chlorine for feldspars. The data on quartz is extremely limited, but the chlorine content may be 30-150 ppm. The chlorine in quartz and feldspars seems to be in the form of brine filled fluid inclusions. The amount of inclusions may depend on the rate of crystallization. If so, this is an additional complicating parameter. In one report on two coexisting quartz-feldspar specimens, the chlorine content in quartz was 50 and 250% higher than in feldspar. Leaching of samples ground to 100 mesh removed 20-40 ppm chlorine. Gillberg (1964) reports that leaching feldspar ground to less than three microns removed all the chlorine but that only 10% of the chlorine was removed from a similarly treated biotite. The nearly unleachable chlorine in biotite may be more leachable at higher temperatures. The chlorine in quartz or feldspar inclusions is leached through kaolinization of the feldspars

possibly assisted by microscopic solid-state diffusion (Verhoogen, 1952), or thermal migration of inclusions (Anthony, 1971). Chlorine is found in all common minerals in granitic rocks. Although biotites are often rich in chlorine, it is not possible to predict which minerals' chlorine content correlates best with coexisting fluids in equilibrium with the minerals. Whole rock analysis was chosen as the primary tool for this thesis. The lack of knowledge on the distribution of chloride within the rock makes this simple approach most suitable until the problem is further studied.

Published whole rock analyses for chlorine by Jones and Huang (1967) and Kuroda and Sandell (1953) are summarized in Table VII. Steuber et al. (1968) revised the estimate for the mantle down to 32 ppm on the basis of probable crustal contamination of many samples. Billings (1967) argues that the value for shale (100 ppm) is low by as much as a factor of 14 due to near surface leaching. Most of the chlorine in fresh shales is water soluble. Fuge and Power (1969) present the only detailed study on chlorine in granitic rocks. They find a log normal distribution of samples with a mean of 507 ppm chloride. Kaolinization releases chloride to a large degree. Such alteration also releases most base metal in the rock. This average chlorine content is higher than the world average for granite. The lack of quantification of the controlling parameters prevent saying more than that high chloride in the source rock should favor high chloride in solutions leaching the rock.

TABLE VII

AVERAGE CHLORINE CONTENTS OF ROCKS (IN PPM)
(Range in Parentheses)

	Jones and Huang, 1967 (Accuracy Not Given)	Kuroda and Sandell, 1950 (Accuracy in This Column ± 10% @ 500 ppm, ± 20% @ 200 ppm)
Meteorites		
Silicate	470 (300-800)	
Iron	200?	
Crust	180	
Mantle	100	
Igneous		200
Ultramafic	100	
Mafic	160	175 (25-450)
Intermediate	180	180 (25-350)
Silicic	200	140 (50-250)
Syenite	430	100-200
Nephelinite	2170	
Granite	(20-500)	220 (50-500)
Granodiorite	(30-500)	
Rhyolite		140 (50-250)

TABLE VII (Continued)

Sedimentary	105	
Shale, Clay	100 (50-450)	
Quartz Sandstone	20	
Limestone	130	200
Dolomite	660 (400-880)	
Graywacke	(12-200)	
Metamorphic		
Schist	350	
Gneiss	200	
Amphibolite	300	

IV. TRANSPORT AND CONCENTRATION

Metals must be extracted or partitioned from the source rock into an aqueous fluid phase to form hydrothermal ores. Igneous intrusives may provide chloride-rich fluid. Depletion of the mantle, enrichment of the crust and oceans, as well as experimental studies, all indicate that chlorine is concentrated in the aqueous phase during the late stages of magmatic crystallization. Iwasaki (1968) found many dunites and peridotites containing under 20 or even 10 ppm chlorine. He concludes that most chlorine leaves the rock in the liquid or gaseous magmatic emanations on solidification of a partial melt. The calculated loss of chloride from the mantle agrees well with the amount of chloride found in the oceans today.

Kilinc and Burnham (1972) have studied the partitioning of chloride between water and granitic or granodioritic melts at equilibrium. At up to six kilobars pressure, the concentration of chloride was over 30 times as great in the aqueous phase as in the solid phase. Over six kilobars, the chloride did not partition as well, but data is lacking beyond eight kilobars. These results were not dependent on melt composition or temperature in the ranges tested (700-750°C).

The concentration of chloride in the aqueous phase is strongly dependent on the water content of the magma (Kilinc and Burnham, 1972). The ratio of chlorine in the aqueous phase to chlorine in the original magma for a water saturated granite ranges from two to 50 depending on, among other things, whether the system was open or closed. At 0.5, 1, and 2 kilobars, the water content of a saturated granite is about 2.7%,

4.3%, and 6.3% respectively. The loss of pressure as a water saturated intrusive nears the surface releases large amounts of water. Whether the system is open or closed, however, 20 or more percent of the total aqueous phase is enriched in chloride by a factor of 30 or more over the original magma.

In some cases, the concentration of chloride rises with the degree of crystallization. Boiling may also concentrate salts a great deal. This can explain the presence of some very concentrated salt solutions found in fluid inclusions in some granitic rocks. In other cases, later release of magmatic water may dilute initial chloride-rich solutions. Nearly typical conditions in the cooling of a large mass of granitic or granodioritic magma can lead to the release of large amounts of water greatly enriched in chloride. Such solutions are capable of dissolving or leaching practical (1-1000 ppm) amounts of base metals with which they come in contact.

As an extension of the lateral secretion theory, the country rocks which supply the metal in that theory may also supply the chloride. Ellis and Mahon (1967) leached greywacke and various volcanic rocks at 400-600°C and 1500 bars for two weeks. Fifteen to 90% of the chlorine was removed from the rock. Most was removed at temperatures as low as 350-450°C. Thus hydrothermal alteration or leaching by water released in metamorphism can also result in chloride-rich solutions. A source of heat and a pressure gradient to transport the fluid are still required. Low chlorine in the rock could represent low original chlorine or it could mean that the extraction efficiency was high. This problem is

exactly analogous to the problem of positive and negative regional metal anomalies discussed earlier. Since chlorine release may be fault or fracture controlled, broad negative chlorine anomalies probably represent low original chloride.

V. FLUID INCLUSIONS

Fluid inclusions provide the only direct form of evidence about fluids which have actually formed ore deposits. Fluid inclusions, if primary, provide us with a minute sample of the fluid which was depositing the ore. If the deposition was due to the loss of a volatile, however, the volatile will not be present in the inclusion.

The most striking feature of some fluid inclusions associated with epigenetic ore deposits is their high salinity, which ranges up to 40%. Roedder (1971) found that with few exceptions, all primary inclusions associated with ore in an East Tennessee district had over 20% NaCl. Nash and Theodore (1971) found that fluid inclusions in or near a porphyry copper deposit in Nevada had a salinity of about 40% whereas inclusions from outlying parts of the deposit or in post ore minerals were of low to moderate salinity. They concluded that the high density of the highly saline fluids might also be an important factor in their localization. Pinckney (1970) found a reasonably good correlation between zinc and chloride concentrations in fluid inclusions from the Cave-in-Rock district in southern Illinois. Settling of dense metal rich brine into basins may localize the resulting ore in this district.

Roedder (1960) concluded from the lack of ore particles in inclusions that ore fluids could not contain over 100 ppm metal. He believes that this concentration is more than adequate to produce known deposits. Actual analyses of fluid inclusions by Pinckney (1970) show 10-1000 ppm zinc and 50-500 ppm copper in one district. The fluid inclusion evidence helps confirm the role of chloride in ore transport.

VI. EXPERIMENTAL

Experimental and theoretical studies clearly demonstrate the large dependence of metal solubilities on chloride concentration (Holland, 1971). Helgeson (1964) constructed numerous computer models of thermodynamic systems involving mainly lead. He predicted lead solubilities of 1-600 ppm at temperatures from 25 to 350°C in concentrated saline solutions. Later Helgeson (1970) included models for copper, zinc, and silver, among others.

Hemley (1967) performed experimental studies which also took into account the buffering effect of wall rock minerals. He measured the solubilities of galena and sphalerite from 300°C to 500°C at 1 kilobar. 0.5 and 2.0 molar KCl solutions were buffered (with respect to K^+/H^+) by K-feldspar-muscovite-quartz or pyrophyllite-muscovite-quartz. This gave pHs of 4.0-4.5 which agree with the observed sericitization, argillization, and pyrophyllization characteristic of wall rock alteration often associated with base metal sulfide deposits. Solubilities ranged from 65-1900 ppm at 300°C to 2000-13,800 ppm at 500°C. The higher chloride concentrations had about twice the dissolved metal. KCl

solutions without the rock buffer dissolved 13 ppm zinc at 300°C and 196 ppm at 500°C. These experimental results agree within a factor of two with the calculated values of Helgeson (1970).

Anderson (1973) experimentally verified some of Helgeson's models at lower temperatures for lead and zinc. Solubilities of galena and sphalerite were both about 60 ppm at 150°C and 2 ppm at 50°C in 3 molar NaCl at pH 4.0. The pHs of fluid inclusions have not yet been accurately measured.

Lavery (1971) calculated from studies of diffusion haloes that the ore-forming fluids in a Wisconsin lead-zinc district must have been well over 35 ppm zinc and more probably about 200 ppm zinc.

Helgeson (1967) provided thermodynamic data which indicates that an arkose containing 100 ppm lead would equilibrate with interstitial sea water containing 1-4 ppm lead at 200-300°C, depending on temperature. The amount of lead released in this model depends on the amount of potassium feldspar altered to kaolinite, chlorite, and quartz. This is the major mineral equilibrium. The model assumes that lead is released to the solution only as a result of alteration. Unless the chemical bond of lead to the feldspar is significantly stronger than the bond of the lead in the chloride complex, short range solid state diffusion (Verhoogen, 1952) or inclusion migration (Anthony, 1971) might add significant lead to the aqueous phase. Given good permeability, these effects could raise the lead content of the aqueous phase by many times in geologically reasonable time.

Experimental evidence for the role of chloride in dissolving metals was well established by Holland (1972). He showed that the partitioning of zinc from silicate melts into an aqueous phase follows roughly the square of the chloride concentration. Reasonable chloride concentrations (2-6 moles/Kg) can give concentrations of zinc in the aqueous phase of 8-72 times that of the silicate phase. This is probably also true for manganese and lead. Other metals were not tested. He concluded from other evidence that most silicic and intermediate magmas contain 1-5% water, most of which is lost on crystallization. The water may be from deep or shallow sources.

VII. FIELD EVIDENCE

Two present day examples of systems producing ore-forming fluids are the Red Sea rift and the Salton Sea geothermal system. Near the Salton Sea, California (Helgeson, 1968), fluids have been found at a depth of several thousand feet with 80 ppm lead, 500 ppm zinc, 3 ppm copper, and about 150,000 ppm chloride. The fluids permeate an arkose overlain by shale. The temperature is over 300°C. Skinner (in Stanton, 1972, pp. 153-66) found 0.8 ppm silver, 8 ppm copper, 84 ppm lead, 790 ppm zinc, and 155,000 ppm chloride as well as sodium, potassium, calcium, etc. in fluids of the same type in the same area. Five to eight tons of a scale containing 20% copper, 1/10 oz. gold per ton, plus several hundred ounces of silver accumulated at one well in three months. This is clearly ore and the fluid is clearly an ore-forming fluid.

Some of the richer sediments taken from the floor of the Red Sea had 21% ZnO and 4% CuO. If this were on the surface, it would be an excellent ore. The brines above the sediments have up to 255,000 ppm NaCl (Bischoff, 1969).

It is not certain how representative these two systems are of the majority of ore-fluid forming systems. It should be noted that both involve hot, chloride rich solutions. They may, in fact, have far more chloride than necessary to dissolve the metals.

APPENDIX B

NEUTRON ACTIVATION ANALYSIS

The problems with neutron activation analysis for chlorine can be largely overcome by use of equipment which was not available. Special counters can raise the maximum count rate from 2-3,000 CPS to about 90,000 CPS by means of pile-up rejection and baseline correction circuits. This alone would reduce the standard deviations due to counting errors to 5-9% which is satisfactory. The samples would require mechanical handling due to their intense radioactivity.

The effective peak to Compton ratios (signal to noise ratios) could be increased by means of gamma-gamma coincidence counting or coincidence-anti coincidence counting. Either of these methods could increase the peak to Compton ratio by a factor of four or more (Bramlitt, 1966; Morrison, 1969). Morrison determined chlorine in the United States Geological Survey standard rocks W-1, BCR-1, AGV-1, and G-2 without chemical separation. The chlorine contents were 50-200 ppm. The standard deviations were not given but appeared to be about 15% with 2.5% sodium present (BCR-1). This would be nearly acceptable for the purposes of this thesis.

Gamma-gamma coincidence counting utilizes the fact that activated chlorine emits 2.15 MeV and 1.60 MeV gamma rays simultaneously when it decays. Two identical counters are used on opposite sides of the

sample and only those events with a 2.15 MeV count in one counter and a 1.60 MeV count on the other are recorded. The method has not been tried on rocks but should work very well.

Because the beta ray emitted in the decay of activated chlorine is one of the most intense known (4.9 MeV), it should be possible to obtain very good results with a beta ray analyzer (Lobanov, 1967). A magnetic field directs beta rays of varying energies into various slits as in mass spectoscopy. This rejects practically all of the gamma and beta rays from sodium and manganese which ordinarily interfere with chlorine.

Additional elements which can often be run together with chlorine with little or no additional effort include sodium, potassium, aluminum, vanadium, magnesium, manganese, and possibly indium, dysprosium, and nickel. Many other elements can be determined in the same sample if a longer period is allowed for radioactive decay. Samples with relatively low sodium to chloride ratios such as quartz are particularly appropriate for neutron activation.